

## PATENT SPECIFICATION

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## (54) HYDROFORMYLATION PROCESS

(71) We, DAVY POWERGAS LIMITED (formerly Power-Gas Limited), a British company, of 8 Baker Street, London, W.1., (formerly of Bowesfield Lane, Stockton-on-Tees, Teesside), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the hydroformylation of an olefinically unsaturated compound to an aldehyde or to aldehyde and alcohol.

Hereinafter, the olefinically unsaturated compound will be referred to for convenience as an "olefin".

According to the present invention a process for hydroformylation of an olefin comprises catalytically reacting the olefin with hydrogen and carbon monoxide in a primary reaction zone so that an aldehyde or aldehyde and alcohol is produced and some olefin remains unconverted, withdrawing aldehyde or aldehyde and alcohol product as vapour along with gases including unconverted olefin aldehyde or aldehyde and alcohol from the primary reaction zone, separating gases thus withdrawn, recycling part of the separated gases including unconverted olefin to a primary reaction zone and hydroformylating part of the unconverted olefin in a secondary reaction zone and separating further aldehyde or aldehyde and alcohol product from the secondary reaction zone without further recycling of the remaining separated gases.

It will be understood from the above that a primary reaction zone will receive original feedstock gases and/or recycled gases including unconverted olefin and will be intended to be operated with a relatively high rate of throughput, separation of the product and recycling of unconverted olefin being effected. A secondary reaction zone will normally operate at a high conversion but will in any case be fed with unconverted olefin from a primary reaction zone and effluent gases will not be recycled. The secondary

zone can thus be regarded as a final stage although effluent gases may be treated further for recovery of olefin should this be desirable.

It will be appreciated that whether an aldehyde alone or aldehyde and alcohol is produced will depend upon the molar ratio of hydrogen to carbon monoxide and the reaction conditions such as temperature, pressure, residence time and type of catalyst employed.

Preferably the olefin has not more than 5 carbon atoms and is, e.g. ethylene or propylene.

A plurality of primary reaction zones can be employed with product removal steps being used after each zone with gas recycle after product removal. Similarly a plurality of secondary reaction zones can be used either in parallel or in series.

It will frequently be found to be convenient to arrange the primary and secondary reaction zones in such a way that the reactants in the secondary reaction zone have a higher residence time than the reactants in the primary reaction zone, and/or that the ratio of catalyst to reactant is higher in the secondary zone, in order to minimise the amount of unconverted reactants present after secondary reaction. In general, conditions are preferably such that 20%—40% olefin conversion takes place in the primary reaction zone and up-to 90% or more in the secondary reaction zone. Thus a good total conversion can be achieved with an adequate throughput although the greater part of the aldehyde produced will be as a result of the reaction in the primary reaction zone.

It is also of advantage to operate the primary reaction zone with a high partial pressure of olefin in excess of the stoichiometric requirement because the rate of reaction is a function of olefin partial pressure.

Product removal will in general be by cooling to liquefy the product and this cooling is beneficial if employed between reaction zones since the hydroformylation reaction is exothermic.

Although the invention is applicable both

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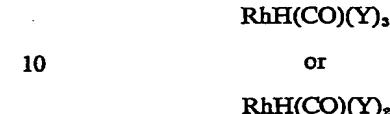
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to heterogeneous and homogeneous catalytic systems, it is primarily intended to be used in reaction to the latter with a liquid catalyst reaction medium containing a hydrido carbonyl complex of rhodium which includes a phosphorus-containing ligand, e.g.



where Y is a triphenyl phosphine or triphenyl phosphite group. The medium is preferably a solution of the complex in free phosphorus-containing ligand material which is the same ligand as that in the complex, with no additional inert solvent.

The olefin can be fed to the primary reaction zone as a gas and it is envisaged that liquid olefin could be injected, with advantage in some cases, into the zone to produce a cooling effect.

The invention will now be described by way of example only, with reference to the Figure accompanying the provisional specification which is a flow diagram of a process for hydroformylation of propylene to produce butyraldehyde.

A mixture of gaseous propylene, hydrogen and carbon monoxide at a pressure above atmospheric is fed through a line 1 to a primary reactor 2 containing a liquid reaction medium consisting of RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> as catalyst and triphenyl phosphine as solvent with varying amounts of product aldehyde, the gaseous mixture being admitted below the surface of the medium in this instance.

The pressure and temperature of the reactor are 180 p.s.i.g. and 125°C respectively. About 30% conversion of propylene takes place and mainly butyraldehydes are produced in the reactor 2 with gases which are in general inert in the reaction conditions and which arise from impurities in the feed gas mixture itself and from side reactions occurring during the main hydroformylation reaction.

A gaseous mixture leaves the upper part of the reactor which mixture consists of inert gases (in relation to the reactants), aldehyde product, and unreacted gases. The reaction conditions are adjusted to cause an appropriate amount of aldehyde to be removed with the inert gases and unconverted reactants. The rate of aldehyde removal depends on the partial pressure of the aldehyde the partial pressures of the inert and feed gases and the rate of input of the feed gases.

The gaseous mixture is passed into a cooler 3 where most of the aldehyde product is condensed and thence to a separator 4. Aldehyde product is removed from the base of the separator, whilst gases consisting of the "inert" gases and a significant

amount of unconverted reactants are withdrawn from the top of the separator through a line 5. A portion of these gases is purged through a line 7, whilst the remaining portion is recycled through a compressor 6 to join, in line 1, the feed gas to the reactor 2.

The purged gas in line 7 passes to a secondary reactor 8 containing a similar liquid catalyst reaction medium to that in the primary reactor 2. Unconverted reactants in the purged gas react in the vessel 8 and the resulting mixture of gases is withdrawn from its upper part. The conditions in the reactor 8 are adjusted so that the gas mixture leaving the vessel 8 mainly consists of inert gases and aldehyde product. The mixture is passed to a cooler 9 where the aldehyde product is condensed. After the cooler the mixture enters a separator 10 where liquid aldehyde product is withdrawn from the base thereof and mainly inert gases from the top.

Should the rate of aldehyde removal from the secondary reactor 8 be less than its rate of formation therein, reaction medium containing aldehyde is withdrawn through a line 11 and delivered to the primary reactor 2 in which aldehyde will be stripped from this recycle medium. At the same time, reaction medium is withdrawn through a line 12 from the reactor 2 and fed to the reactor 8 to maintain the quantity in each reactor constant.

If there was no secondary reactor and the gas stream from a main reactor were recycled, after aldehyde removal, to the main reactor, then a build-up of "inert" gases would occur in the system. If the recycle stream were purged to overcome this build-up there could be serious loss of olefin. The use of a secondary reactor after aldehyde removal minimise these difficulties.

The process enables the bulk of the product aldehyde to be removed from the reactor 2 very soon after it is formed. If product aldehyde remains in contact with the hydroformylation catalyst in the presence of hydrogen the aldehyde tends to be hydrogenated to alcohol. By operating in the manner described the residence time during which catalyst, aldehyde and hydrogen are all in contact together is relatively short, and thereby alcohol production is minimised.

In the example described the reactors were charged with equimolar proportions of H<sub>2</sub>:CO and olefin. This is the stoichiometric requirement for aldehyde production. It may be found convenient to use different proportions of reactants in the primary reactor in order to optimise the reaction rate and/or minimise unwanted side reactions. If this is done the composition of the reactants passing to the secondary reactor can be adjusted to approach the stoichiometric requirements by the addition of CO, hydrogen, or olefin. More often the primary reactor will be

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- charged with reactants rich in olefin and additional synthesis gas ( $\text{CO} + \text{H}_2$ ) added before the secondary reaction zone.
- It is not essential that the primary and secondary reaction zones are operated at substantially the same pressure. In some cases an advantage can be secured by operating the secondary reactor at a high pressure by the use of a compressor in the purge stream in line 7. This increases the partial pressures of the reactants and consequently also their rate of reaction or degree of conversion.
- 15 WHAT WE CLAIM IS:—**
1. A process for hydroformylation of an olefin comprising catalytically reacting the olefin with hydrogen and carbon monoxide in a primary reaction zone so that an aldehyde or aldehyde and alcohol is produced and some olefin remains unconverted, withdrawing aldehyde or aldehyde and alcohol product as vapour along with gases including unconverted olefin from the primary reaction zone, separating aldehyde or aldehyde and alcohol from the gases thus withdrawn, recycling part of the separated gases including unconverted olefin to a primary reaction zone and hydroformylating part of the unconverted olefin in a secondary reaction zone and separating further aldehyde or aldehyde and alcohol product from the secondary reaction zone without further recycling of the remaining separated gases.
  2. A process for hydroformylation as claimed in claim 1 wherein the residence time of the reactants and/or ratio of catalyst to reactants is higher in the secondary reaction zone than in the primary reaction zone.
  3. A process as claimed in claim 1 or claim 2 wherein separation of the product is effected by cooling and liquification of the aldehyde and/or alcohol product.
  4. A process as claimed in any of claims 1 to 3 in which the olefin has not more than 5 carbon atoms.
  5. A process as claimed in claim 4 in which the olefin is ethylene or propylene.
  6. A process as claimed in any one of the preceding claims in which additional reactant, e.g. synthesis gas, is passed into the secondary reaction zone to provide a feed to the zone approaching a stoichiometric mixture.
  7. A process as claimed in any one of the preceding claims in which a partial exchange of liquid catalyst material containing the aldehyde or aldehyde and alcohol product in solution from the secondary reaction zone and liquid catalyst material from the primary reaction zone is effected.
  8. A process as claimed in any one of the preceding claims in which the primary reaction zone is operated with a feedstock containing olefin at a high partial pressure in excess of the stoichiometric requirement.
  9. A process as claimed in any one of the preceding claims in which one or both of the primary and secondary reaction zones includes a liquid catalyst reaction medium containing a hydrido carbonyl complex of rhodium which includes a phosphorus containing ligand such as  $\text{RhH}(\text{CO})(\text{Y})_3$  or  $\text{RhH}(\text{CO})(\text{Y})_2$  where Y is a triphenyl phosphine or triphenyl phosphite group, preferably in solution in a similar free phosphorus containing ligand material such as triphenyl phosphine.
  10. A process as claimed in any one of the preceding claims in which the secondary reaction zone is operated at increased pressure by the provision of a compressor in the purge supply line from the separator for the products of the first reaction zone.
  11. A process for hydroformylation of an olefin substantially as described herein.

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